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(54) COMPOSITE MATERIAL CONTAINING HARD METAL CARBIDE PARTICLES, AND METHOD FOR THE PRODUCTION THEREOF

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organized under the laws of the Netherlands, of 30, Carel van Bylandtlaan, The Hague, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a composite material containing hard metal carbide particles. Further, the invention relates to a method for producing such composite material and for production of a body consisting of such materal.

Composite materials containing particles of hard metal carbide (such as tungsten carbide, titanium carbide and molybdenum carbide) bonded together by a softer binder have been used over already a long period in the manufacture of oil field drill bits, machine tools and similar articles which are subjected during operations to considerable erosion and/or wear such as abrasive and/or mechanical wear.

Such composite materials are normally produced by placing hard metal carbide particles in a suitable mould, vibrating the mould to obtain a closely packed mass of particles therein, adding pellets of a binder metal capable of wetting the metal carbide particles in the molten state, and thereafter heating the mould and its contents to an infiltration temperature above the melting point of the binder metal. As it approaches this temperature, the molten binder flows downwardly into the interstices between the metal carbide particles. As a result thereof, a bond is formed at the surfaces of the particles between the binder and the particles. The composite material obtained after cooling and solidification of the binder consists of a mass of particles bonded together by a continuous binder phase. Since the particles have a high density and are moreover closely packed, the composite material thus obtained is of high density. These materials generally show a good resistance against erosion as well as against mechanical and/or abrasive wear.

However, composite materials have at present to be used under extreme conditions, where the available types of materials fail to meet the requirements on resistance against erosion and/or wear.

An object of the invention is a composite material that shows a remarkable resistance against erosion and/or wear.

A further object of the invention is a method for the production of such a material.

According to the invention, such method comprises the steps of filling a mould with a mass of hard metal carbide particles of a first sieve fraction, vibrating the mould to compact the mass of particles, adding on top of the compacted mass of particles a mass of hard metal carbide particles of a second sieve fraction, the particles of the second sieve fraction being smaller than the particles of the first sieve fraction to an extent sufficient to allow them to infiltrate the interstices of the compacted mass of particles of the first sieve fraction when vibrating the mould, vibrating the mould to infiltrate said interstices with the particles of the second sieve fraction, and thereafter infiltrating the interstices of the mass of particles thus compacted with a molten metal binder, and cooling the mould and the contents thereof.

The first sieve fraction may be between 100 mesh and 3 mesh, whereas the nominal diameter of the particles of the second fraction may be between 10^{-3} millimetres and 0.5 millimetres. By "nominal diameter" of a particle is herein to be understood the diameter of a sphere having the same volume as the particle.

In an attractive embodiment of the invention, the first sieve fraction is between 20 mesh and 10 mesh, whereas the second sieve fraction is between 270 mesh and 100 mesh.

The smallest particles of the first sieve fraction may have a size that is at least four times the size of the largest particles of the second sieve fraction.

A third, fourth or even a fifth sieve fraction may be used. Each following sieve fraction consists of particles that are smaller than the particles of the preceding sieve fraction. The smallest particles of the second sieve fraction may have a size that is at least three times the size of the largest particles of the third sieve fraction.

For improving the degree of compaction of the particles, the mould may be vibrated horizontally and consecutively in a plurality of directions.

The composite material obtained by the method according to the invention comprises a compacted mass of large-sized particles of the first sieve fraction, said mass having the interstices thereof filled up with a compacted mass of small-sized particles of the second sieve fraction. The volume not occupied by particles is filled up by metal binder.

The composite material of the invention shows an extremely high carbide-density since the consecutively compacting of two separate sieve fractions of particles leads to an extremely high final compaction, which may well be over 80%. This material with high carbide-density has been found to show an improved resistance to erosion as compared to composite materials having the hard metal carbide particles incorporated therein belonging to a single sieve fraction only.

A body of composite material according to the invention and having a wall with large resistance to abrasive and/or mechanical wear may be obtained by grinding at least part of that wall of the composite material body that has faced a wall of the mould, over a depth equalling about 10 to 50% of the mean value of the widths of the maximum mesh and the minimum mesh of the first sieve fraction. The ground surface exposes a cross-section over particles, the area of the cross-section being at least 75% of the area of the surface. It will be appreciated that this large percentage of the area occupied by the hard metal increases the resistance to erosion and wear to a great extent. Consequently, such surface is ideal for forming a slidable barrier between two zones of different pressure, as is required in pumping equipment, etc.

The invention will now be described by way of example in more detail with reference to some Examples and to the drawing accompanying the provisional specification which shows a magnification of a top view on a surface of a composite material according to the invention.

Where the fractions of the particles are within the ASTM-range, they are indicated in this range. In those cases where one of the boundaries is outside the ASTM-range, the boundaries will be indicated by the nominal diameter of the smallest and the largest particle of the fraction. By "nominal diameter" of a particle is herein to be understood the diameter of a sphere having the same volume as the particle.

Further, it will be appreciated that without departing from the scope of the invention, a small percentage (say 5 to 10%) of the particles of a fraction may be outside the fraction boundaries indicated.

EXAMPLE I

A mass of tungsten carbide particles of a first sieve fraction ranging from 20 to 18 mesh, and weighing 265 grams is deposited in a mould consisting of compressed carbon powder (and having an inner volume of about 27 cm^3).

After the mould has been filled with the particles, the mould is horizontally vibrated at about 50 vibrations/second during about 5 minutes. The main direction of vibration is varied several times during this vibration operation, which finally results in an apparent density of the mass of particles (also referred to as tap density) of about 58%.

Subsequently, a mass of tungsten carbide particles of smaller dimensions (sieve fraction ranging from 120 to 100 mesh) and weighing 70 grams is deposited on the compacted mass of relatively large particles, and the mould is again horizontally vibrated during about 30 minutes. The direction of vibration is changed several times and the small-sized particles enter into the interstices of the already compacted mass of large-sized particles. Since the vibration movements are in a horizontal plane, the already compacted mass stays compacted and the small-sized particles are distributed over the interstices of the large-sized particles and form a compacted mass therein. The apparent density of the compacted mass of tungsten carbide particles thus obtained is found to be 75%. It is observed that the smallest particles of the first sieve fraction have a size that is at least four times the size of the largest particles of the second sieve fraction.

The mould with the particles is thereafter placed in a furnace, whereafter a metal binder (consisting of a composition of Ag, Cu, Zn and Cd and having a melting temperature of 650°C) is allowed to flow into the interstices of the particles (said interstices having a volume of 25%). Upon removal of the mould from the furnace, the composite material is allowed to cool down, whereafter the body is removed from the mould. The composite material has a density of about 14.2 g/cc. The resistance to

erosion is tested by impingement of a high velocity mud jet perpendicular to the surface of the body during a pre-determined time interval. The susceptibility of the body against erosive action is defined by the depth of the hole resulting from the jet action.

Test data:	
jet nozzle diameter	3 mm
distance between body and nozzle outlet	3 mm
pressure drop over nozzle	155 kg/cm^2
ambient pressure	45 kg/cm^2
exposure time	15 minutes
Mud composition:	
1000 litre water	
400 kg Limburgia (sand)	
60 kg bentonite	
Test result:	
average hole depth	0.35 mm

EXAMPLE II

A mould filled with compacted tungsten carbide particles having sieve fractions ranging between 14 and 10 mesh (first sieve fraction), and between 60 and 50 mesh (second sieve fraction) is made up in the manner described with reference to Example I. Since the size of the smallest particles of the first sieve fraction is more than four times the size of the largest particles of the second sieve fraction, infiltration time of the second sieve fraction into the compacted first sieve fraction is not excessively long. Prior to heating the mould and its contents, a third amount of tungsten carbide particles of a sieve fraction from 270 to 200 mesh is infiltrated by vibration into the interstices of the compacted particles of the other two fractions. Since the size of the smallest particles of the second sieve fraction is more than three times the size of the largest particles of the third sieve fraction, infiltration time will not be too long. The mould is vibrated horizontally in various directions, and an interstice volume is reached that is 20—15% of the total volume of the packed particles. After heating and addition of molten binder (a Cu-Mn 12 composition), a specific density of about 15 g/cc of the body of composite material is obtained. Erosion tests carried out in the manner described with reference to Example I gave an average hole depth of 0.25 mm.

EXAMPLE III

The body of composite material described in this example is in particular adapted for use at locations where high requirements are set for the resistance against abrasive forces. Such body is manufactured by grinding a wall (such as the bottom surface) of the body of composite material obtained by the method described in Example II. The bottom surface of the body has faced the bottom of the mould during the period over which the mould has been vibrated. As a result of such vibration, the particles of the first sieve fraction are positioned on the bottom of the mould in a manner such that the degree of contact between the surfaces of these particles is highest in the region that is situated at a distance from said bottom that is between 10 and 50% of the mean value of the widths of the maximum mesh and the minimum mesh of the first sieve fraction. Thus by grinding the bottom surface of the body away over a depth that is between 10 and 50% of said mean value, the cross-sectional surface thus exposed shows a relatively large area thereof occupied by cross-sections of the large-sized tungsten carbide particles. A magnification of a top view of this surface is schematically shown in the drawing. Particles of the first sieve fraction are indicated by reference numeral 1, whereas particles of the second and third sieve fractions are indicated by numerals 2 and 3, respectively.

In this example, the surface has been ground over a depth of about 20% of the said mean value. The area of the cross-sections of the particles 1 forms 78% of the total area of the ground part of the body surface. Further, 12% of the total area is formed by the cross-sections of the particles 2 and 3, whereas the remaining 10% is a cross-section over the binder metal.

It will be appreciated that a surface comprising such an extremely large carbide area will show an excellent resistance against abrasive and/or mechanical wear. Such surface will therefore be useful for application in equipment comprising surfaces that should form a slidable seal to separate zones of different pressure and containing abrasive fluids.

Further, the resistance to erosive action of the ground surface is extremely high. An average hole depth of 0.25 mm was measured under test conditions equal to those described in Example I.

Improved resistance against abrasive and/or mechanical wear of a surface of a body according to the invention may also be obtained by grinding a surface or a plane other than the surface or plane of the body that has faced the bottom of the mould thereof. However, the top plane is not suitable for this purpose. These other planes or surfaces are then ground over a depth equal to 10—50% of the mean value of the widths of the maximum mesh and the minimum mesh of the first sieve fraction, in the same manner as described with reference to the bottom surface. However, the results obtained are not as good as

reached when grinding the bottom plane or surface over an equal depth.

The improved resistance to erosive action of the composite material according to the invention is made clear by the tests referred to in the examples. It is believed that this improved erosion resistance may be explained as follows. As a result of the consecutive compaction of the masses of particles of diminishing particle sizes, a high carbide density and consequently a small pore volume is obtained. However, the number of pores has increased greatly by the use of the particles of the second and further sieve fractions. The individual pores have a slender configuration, and consequently any liquid jet trying to dislodge particles from the mass that is bonded together by the binder metal in the pores, has to erode this binder metal from slender pores, which due to this configuration destroy the jet-energy before the jet can protrude beyond the separate particles to dislodge them from the composite material. The erosion of the metal binder than stops and the resistance to erosion is solely dictated by the hard metal particles.

The resistance to erosion of a composite material differing from the material of Example I only in that the hard metal particles were of a sieve fraction between 120 and 18 mesh was found to be considerably lower than the erosion resistance of the material according to Example I. It is observed that this single sieve fraction spans all particle sizes between the smallest mesh size of the first sieve fraction and the largest mesh size of the second sieve fraction of the particles applied in Example I. The particles of this single sieve fraction were compacted in the mould by vertical vibration. Comparative erosion tests showed an average depth of about 3 mm of the single sieve fraction material against 0.35 mm of the Example I material.

Similar low erosion resistance was found in a body made of a composite material comprising the sieve fractions as used in Example III, which sieve fractions, however, had been vertically vibrated in the mould simultaneously for compaction purposes. The area of the ground plane that was occupied by binder metal was found to be 35% of the total area of the ground plane. The erosion resistance was found to be about 3 mm in the tests similar to those described with reference to Example III.

All types of hard metals may be applied in the present invention. The same applies for the binder metal, provided that this metal (or composition of metals) has the ability to wet the surfaces of the particles, to infiltrate into the interstices thereof, and to form a bond with the particles. The melting temperature should be sufficiently low to prevent destruction of the desirable properties of the hard metal. Also, if the composite material should be applied for hard surfacing metal bodies, the above properties of the binder metal should also apply to the metal or metal compositions of which the metal body is made.

One important advantage of the extremely high grade of compaction that can be obtained by the method of the invention should still be mentioned. This advantage relates to the extremely low amount of shrinkage of the composite material that occurs during cooling down of the mould. This may be explained by the following. The metal binder has a large coefficient of contraction when cooling down and therefore induces reorientation of the particles in those composite materials wherein the large-sized particles are inadequately compacted. In the composite material of the present invention, however, these particles are compacted in such a manner that they are immobile. Moreover, per unit length, only a small number of large-sized particles will be in contact with each other. Consequently no significant re-orientation of the large-sized particles will occur during cooling down of the binder metal and shrinkage will be negligible.

A composite material with an attractively low shrinking coefficient will be obtained when applying large-sized particles in the first sieve fraction that are larger than about 0.3 mm (50 mesh).

A hard composite material with low-shrinking coefficient will be extremely useful in forming an abrasive resistant outer body layer of a diamond bit, in which layer diamonds have to be placed. Damage of diamonds by cracking due to shrink of the body layer during manufacture is then obviated. The life of the diamonds will further be prolonged by applying a binder material with low melting temperatures. Such composite material will be described in the following example.

EXAMPLE IV

Tungsten carbide particles of a first sieve fraction between 18 and 14 mesh are vibrated horizontally in a mould made of compressed graphite. Diamonds have been glued in the mould at appropriate places prior to vibrating the mould. The mould is vibrated horizontally in a direction that is varied several times to increase the degree of compaction of the particles. Subsequently, a perforated plate (or sieve) is pressed on the upper surface of the particles in the mould, the perforations having a diameter of a size between the first and the second sieve fractions. A batch of small-

sized tungsten carbide particles of the second sieve fraction is then placed on the plate, and the assembly is vibrated in a plurality of directions consecutively, these directions not particularly lying in a horizontal plane. The small-sized particles (of a sieve fraction between 80 and 60 mesh) infiltrate into the interstices of the compacted mass of relatively large-sized particles, until the desired degree of compaction is obtained in the interstices. The remainder of the small-sized particles left on top of the perforated plate is thereafter removed (together with the plate), and a metal binder consisting of a composition of silver, copper, zinc and cadmium is subsequently placed in small lumps on the top of the particle pack in the mould. Heating the mould and its contents in a furnace up to a temperature of 670°C and subsequent cooling results in a body of composite material having the diamonds embedded therein and showing no significant shrinkage.

In order to obtain a good bond between the particles and the binder metal, it is advantageous to coat the particles with a suitable coating metal. In this particular example, the particles are coated by a nickel layer of about 0.2 micron by an electrolytic process. Instead the particles may be coated with copper or cobalt, if desired.

The properties of the diamonds are not negatively effected by applying the present technique of producing a matrix material, since the material did not show shrinkage during its manufacture which manufacture moreover took place at a moderate temperature (below 800°C).

The method according to the invention further includes the application of additional sieve fractions (say a fourth and a fifth sieve fraction) of diminishing particle sizes, that are consecutively added to the compacted mass of particles of larger size. The particles of each following sieve fraction should be smaller than the particles of the preceding sieve fraction and be chosen to infiltrate the interstices of the preceding sieve fractions upon vibration of the mould with a reasonable time.

Further, the hard metal carbide particles used may be a mixture of different compositions. Also, the compositions of the various sieve fractions may differ from each other.

Finally, an erosion-resistant, abrasive material can be obtained by application of the present invention by replacing at least part of the hard metal carbide particles of the second (and/or a further) sieve fraction by diamond particles of sizes that are within the range of said sieve fraction(s). The diamond particles are then distributed by vibration over the interstices of the compacted mass of hard metal carbide particles of larger dimensions and the body obtained after infiltration with a molten binder followed by cooling, will in addition to abrasive properties, also show a resistance against erosion. This allows the body when applied for cutting purposes, to be subjected to the erosive action of high-velocity liquid jets for cooling and removal of cuttings from the cutting edge of the body.

WHAT WE CLAIM IS:—

1. Method for the production of a composite material containing hard metal carbide particles, said method comprising the steps of filling a mould with a mass of hard metal carbide particles of a first sieve fraction, vibrating the mould to compact the mass of particles, adding on top of the compacted mass of particles a mass of hard metal carbide particles of a second sieve fraction, the particles of the second sieve fraction being smaller than the particles of the first sieve fraction to an extent sufficient to allow them to infiltrate the interstices of the compacted mass of particles of the first sieve fraction when vibrating the mould, vibrating the mould to infiltrate said interstices with the particles of the second sieve fraction, and thereafter infiltrating the interstices of the mass of particles thus compacted with a molten metal binder, and cooling the mould and the contents thereof.

2. Method according to claim 1, wherein the mould is vibrated horizontally and consecutively in a plurality of directions.

3. Method according to claim 1, wherein the mould is vibrated horizontally in any direction after being filled with the particles of the first sieve fraction, whereafter a perforated plate is pressed on top of the compacted mass of particles prior to adding the particles of the second sieve fraction.

4. Method according to any one of the claims 1—3, wherein the smallest particles of the first sieve fraction have a size that is at least four times the size of the largest particles of the second sieve fraction.

5. Method according to any one of the claims 1—4, wherein the largest particles of the first sieve fraction are larger than 0.3 millimetre.

6. Method according to any one of the claims 1—5, wherein the first sieve fraction is between 100 mesh and 3 mesh, and the nominal diameter of the particles of the second fraction is between 10^{-3} millimetres and 0.5 millimetres.

7. Method according to claim 6, wherein the first sieve fraction is between 20 mesh and 10 mesh, and the second sieve fraction is between 270 mesh and 100 mesh.

8. Method according to any one of the preceding claims, wherein a body is removed from the mould after cooling

down, and at least part of the surface of said body that has faced a wall of the mould is ground over a distance of a value between 10—50% of the mean value of the widths of the maximum mesh and the minimum mesh of the first sieve fraction.

9. Method according to any one of the preceding claims, wherein the particles have a coating of nickel, copper or cobalt.

10. Method according to any one of the preceding claims, wherein a mass of hard metal carbide particles of a third sieve fraction is vibrated into the interstices left between the compacted mass of particles of the first and the second sieve fractions, the particles of the third sieve fraction being smaller than the particles of the second sieve fraction.

11. Method according to claim 10 wherein, the size of the smallest particles of the second sieve fraction is at least three times the size of the largest particles of the third sieve fraction.

12. Method according to any one of the preceding claims, wherein at least part of the particles of the second or further sieve fraction is replaced by diamond particles.

13. Method for the production of a composite material, substantially as described with reference to Example I, II and IV of the specification.

14. A body of composite material prepared by the method as claimed in any one of the preceding claims, comprising a compacted mass of relatively large-sized hard metal carbide particles having the interstices thereof filled up with a compacted mass of relatively small-sized hard metal carbide particles, and metal binder filling up the volume not occupied by particles.

15. Body of composite material according to claim 14 comprising one wall thereof at least partly ground to expose cross-sections over the relatively large-sized particles, the total area of the cross sections being at least 75% of the ground area of the wall.

16. Body according to claim 14 or 15, wherein the wall is ground over a depth equal to 10—30% of the mean value of the widths of the maximum mesh and the minimum mesh of the sieve fraction of the relatively large-sized particles.

17. Body of composite material, substantially as described with reference to Example III of the specification.

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